

Oxidation of activated carbon with aqueous solution of sodium dichloroisocyanurate.
Effect on ammonia adsorption.

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Abstract

An activated carbon has been oxidized with 1-10 wt% aqueous solutions of sodium dichloroisocyanurate (DCI) to introduce oxygen and chlorine surface groups by chemisorption; the formation of chlorine surface groups is important when the concentration of DCI is high, the modification of the microporosity being small. The range of stability of the groups is wide, from groups decomposing at high temperature to HCl to those groups decomposing simultaneously to HCl and CO at low temperature. The carbon with the highest degree of oxidation was heat treated under propene at 200-300°C, this facilitating the removal of chlorine groups; thus, all chlorine groups are lost at 250°C, even those thermally stable up to 800-900°C. The effect of both treatments on both the hydrophilicity and the capacity to retain ammonia has also been studied. Oxidation increases the hydrophilicity of the carbon, as shown by the evolution of water adsorption and the enthalpy of immersion into water. On the other hand, oxidation increases the removal capacity of ammonia both at equilibrium and dynamic tests. However, the contribution of the chlorine surface groups on the adsorption of water and ammonia is small, the groups decomposing to CO₂ upon temperature programmed decomposition playing a more important role in the retention of both species.

Keywords: activated carbon; ammonia removal; chlorination; functional groups; propene treatment.

1. Introduction

The surface groups of activated carbon play an important role in the retention at room temperature of polar molecules such as ammonia when diluted in air [1]. The amount adsorbed under these conditions by physisorption (van der Waals forces between the wall of the pore and the ammonia molecules) is very low, oxidation being a common

method to increase the surface acidity of the carbon by introduction of surface groups responsible for more specific adsorption forces.

Of the surface groups produced along oxidation those involving C-Cl bonding have not been explored in depth; they are commonly introduced by reaction of the carbon with chlorine at moderate temperatures [2,3]. However, the number of studies on oxidation of activated carbon with low cost chemicals such as sodium hypochlorite is scarce and they are mainly devoted to the characterization of the resulting oxygen surface groups but not to chlorine groups [4,5]. Additionally, hypochlorite reacts very fast with the carbon particle, thus making the oxidation of the internal carbon atoms more difficult.

The use of organic compounds able to liberate chlorine more slowly could reduce the lack of homogeneity of the oxidation of the carbon particle. This also opens the possibility of forming C-Cl bonds in a simpler way than the treatment of the carbon with chlorine gas. One of the organic compounds more commonly used for chlorination in water treatment and sanitizing applications is sodium dichloroisocyanurate, DCI, (Figure 1); it is soluble in water and it is considered to be a source of free chlorine. Since the equilibrium constant governing the hydrolysis of the N-Cl bonds in the ring is not high [6], the concentration of chlorine in water may remain practically constant if the oxidation time is not too long. DCI has also been used as chlorinating agent to condition the surface of natural and synthetic rubber by adding chlorine to a C=C double bond in the surface and creating C-Cl and C-O bonds [7]. No references were found for the use of DCI or similar compounds in the oxidation of activated carbon.

Ammonia is a dangerous gas for the human being and the design of efficient activated carbon in the purification of air when the concentration of ammonia is low is under

investigation by many research groups [1]. In this application the amount of gas adsorbed by activated carbon is small and, consequently, the surface of the carbon must be modified to increase the specific interaction with the ammonia molecules.

The main objective of this work was to study the modification introduced in the porosity and functionality of an activated carbon oxidized with aqueous solutions of DCI. The effects of the treatment on the hydrophilicity of the carbon and on the capacity to retain ammonia were also to be studied.

2. Experimental

2.1 Preparation

A granular activated carbon (F) with particle size around 1 mm was prepared by physical activation of carbonized olive stones according to a procedure already described [8]. Briefly, the precursor is carbonized for 2 hours under a flow of nitrogen at 850°C and the resulting char was later reacted with a flow of carbon dioxide at 825°C for 48 hours to reach a 52wt% burn-off.

Oxidation of the carbon was carried out as follows: 10 g of carbon F were added to a container with 50 ml of a freshly prepared aqueous solution of DCI ($\text{NaC}_3\text{N}_3\text{Cl}_2\text{O}_3$, Aldrich 96%) at 25°C; the mixture was placed in an ultrasonic bath to facilitate the access of the solution to the interior of the carbon particles. After 10 min the carbon was repeatedly washed with distilled water to ensure the removal of the DCI adsorbed and then dried overnight at 110°C. Four different concentrations of DCI (1, 2.5, 5 and 10%) were selected to produce the carbons listed in Table 1.

In order to partially remove the surface functional groups formed along the treatment with DCI, carbon F10 was treated for one hour under a flow of propene (100 mL/min) at 200, 250 and 300°C. The heating and cooling stages were carried out under a nitrogen flow. The treatment temperature is included in the nomenclature of the samples (see Table 1).

2.2 Characterization

The adsorption of nitrogen at -196°C and carbon dioxide at 0°C was carried out in a home-made high precision volumetric system. Samples were outgassed under vacuum (10^{-1} Pa) at 150°C for 4 hours. The Dubinin-Radushkevich equation was used to deduce the total volume of micropores, $V_0(\text{N}_2)$, and the volume of narrow micropores, $V_0(\text{CO}_2)$, as described in reference [9].

Temperature programmed decomposition (TPD) has been used to study the surface functionality of the carbons. XPS and FTIR were additionally used for some of the carbons. For TPD analysis 100 mg of carbon were placed in quartz reactor under a flow of helium (50 mL/min) and then heated at 10°C/min up to 1000°C. The gases produced along the decomposition of oxygen and chlorine groups were analyzed with a mass spectrometer (Omnistar TM, Balzers). The profiles for CO and CO₂ evolved were integrated using CaC₂O₄.H₂O as standard to determine the amounts evolved for each carbon. The only species evolved for chlorine groups were mainly mass 36 and somewhat less of 35; this means that the groups decompose mainly to HCl.

XPS spectra were obtained in a VG-Microtech Multilab 3000 spectrometer. The source for X-rays was Mg K α . The FTIR spectra were obtained in the range 4000-400 cm⁻¹

using a Bruker IFS 66 spectrometer equipped with a detector DLaTGS in the transmission mode. The samples were diluted in KBr at 5wt%.

2.3 Immersion calorimetry and adsorption of H₂O and NH₃

The enthalpy of immersion into water was determined at 29°C in a Tian-Calvet C80D (Setaram) calorimeter. Samples were previously outgassed under vacuum at 150°C for four hours. More details about the experiments can be found in [10].

The adsorption isotherms at 25°C for water and ammonia were obtained in an automatic volumetric system (Omnisorb 100CX) working at 41°C. Outgassing of the samples was carried out as in the case of the adsorption of nitrogen and carbon dioxide.

The dynamic adsorption of ammonia at 22°C was carried out in a 1cm diameter column containing a 2 cm bed of the carbon. A flow of 300 mL/min of air containing 1000 ppm of NH₃ was passed through the column and the concentration of ammonia was determined using a Polytron 3000 (Drager) detector, with a precision of 0.5 ppm of ammonia and a high detection limit of 500 ppm. The breakthrough of the column was taken when the flow of effluent reached a concentration of 100 ppm ammonia.

3. Results and discussion

3.1 Characterization

Oxidation of carbon F produces an increase in weight (Δm in Table 1) with increasing concentration of DCI, due to the formation of surface groups. The value for F10 is high, thus indicating the effectiveness of DCI as oxidant. There is also a parallel decrease in the volume of micropores because there is an increase in weight but the heteroatoms do not contribute to the adsorption of gases. In fact, when the values of $V_0(\text{CO}_2)$ are

expressed as volume per gram of carbon free of chlorine and oxygen (using the data for Δm in Table 1) the values for samples F2.5, F5 or F10 become coincident with the value for carbon F, $0.42 \text{ cm}^3/\text{g}$. When the same is applied to the total volume of micropores $V_0(\text{N}_2)$ the values are $0.48\text{-}0.49 \text{ cm}^3/\text{g}$, somewhat lower than for carbon F ($0.53 \text{ cm}^3/\text{g}$). In other words, the presence of surface groups formed upon oxidation produce a small narrowing of wide micropores, without affecting narrow micropores. This means that DCI reaches the interior of the carbon particles down to the entrance of the micropores, where it reacts with the more active carbon atoms (those of the edges of the graphene layers constituting the walls of the pores), producing a slight narrowing of the micropores, but without blocking them. Should blocking occur an important decrease in both values of micropores volume would then be observed.

The TPD profiles for the carbons are found in Figure 2, where it is shown that all carbons have groups decomposing to CO_2 , CO and HCl, the amount increasing with the concentration of DCI used in the oxidation process. Figure 2a shows that there is a well defined peak for CO_2 , with a maximum around 280°C . There are also peaks for CO and HCl (Figures 2b and 2c) at that temperature. A strong evolution of CO and HCl in the $350\text{-}900^\circ\text{C}$ range is also observed.

The evolution of CO_2 , CO and HCl indicates that DCI introduces oxygen and chlorine upon oxidation of the carbon. Oxygen is strongly bound to carbon and it can evolve only when there is a rupture of the C-C bond; in the case of chlorine, the bond to be broken is C-Cl and chlorine escapes as HCl. Studies on gas phase chlorination of carbon [4] have shown that the thermal decomposition of the C-Cl surface groups produces the emission of HCl.

The shape of the profiles in Figure 2 indicates a wide range of thermal stability of the functional groups, although two different classes can be distinguished: i) One class, the decomposition of which occurs at low temperature (around 280°C), producing CO₂, CO and HCl. Figure 2c shows that the surface groups evolving as HCl are significant only in F5 and F10, i.e., when the concentration of DCI used is high; this is different to what is seen in Figure 2a, where the amount of groups evolving as CO₂ is high in F1 and increases less with DCI concentration than groups evolving as HCl; ii) The second class corresponds to functional groups decomposing as from 350-400°C, with emission of CO and HCl (Figures 2b and 2c); very wide peaks are observed, thus indicating different bonding strengths between carbon and oxygen or chlorine. These wide peaks are displaced to lower temperatures as the concentration of DCI used in the oxidation increases. This means that the oxygen and chlorine functional groups formed when the concentration of DCI increases are less and less stable.

XPS has been used to study the chlorine surface groups and Figure 3 shows the Cl_{2p} spectrum for the more oxidized carbon F10; deconvolution leads to two peaks of binding energy of 199.9 and 201.4 eV. Since the intensity ratio is 1:2 and both peaks are separated by less than 1.8 eV one can assume that there is only a simple site of chlorine, which produced distinct peaks due to 2p_{1/2} and 2p_{3/2} spectral lines. Papier et al. [11] have followed the chlorination of carbon black with chlorine at 450°C and the peak they found for Cl_{2p} was more complex since deconvolution led to five peaks, the more important one at 200 eV attributed to chlorine atoms covalently bonded to sp² or sp³ carbon atoms. The similarity in binding energy values for carbon black and activated carbon can be taken as an indication of our carbons having direct C-Cl bonds but no C-

O-Cl bonds, since the binding energy for 2p electrons in oxychlorinated groups such as ClO_3^- and ClO_4^- is much higher.

FTIR data also indicate the presence of C-Cl bonding. Figure 4 compares the spectra for carbons F and F10, both being similar and typical of activated carbon [12]. Only to mention here two important differences: i) the band between 1700 and 1730 cm^{-1} , that can be assigned to the stretching vibration of C=O bonds, characteristic of carboxylic groups [13], is much higher in F10 than in carbon F; and ii) new bands at 1400 and 540 cm^{-1} can be seen in carbon F10 as due to functional groups with C-Cl bonds. Bands similar to these have been described in halogenated hydrocarbon polymers [7,14].

The results described above permit to envisage the oxidation of carbon F as follows: the DCI is very soluble in water and the solution containing the anion penetrates in the interior of the carbon particle, helped by the ultrasonic bath. Only part of DCI is transformed into dihydroisocyanurate and chlorine since the equilibrium constant for the hydrolysis of the N-Cl bonds is not high [6], although the additional formation of chlorine induced by sonication is not discarded. The chlorine formed reacts with water leading to HClO in equilibrium with ClO^- . Consequently, a solution containing a complex mixture of equilibrium species is filling the pores, the species chlorine and hypochlorous acid reacting with the carbon atoms. Given the rapid equilibrium among species, one can predict the simultaneous chemisorption of chlorine and oxygen on the unsaturated (more active sites) carbon atoms of the structure. Furthermore, the similarity of the TPD bands in Figure 2 and their evolution with increasing oxidation indicates that both chlorine and hypochlorous acid compete for the same active sites of the adsorbent and, consequently, the relative proportion of oxygen and chlorine surface groups will be a function of the conditions used for the oxidation.

Figure 2 shows that the amount of oxygen and chlorine surface groups decomposing at low temperature increases with the concentration of DCI. However, when the concentration of DCI is low (for instance, compare carbons F and F1) the increase in groups decomposing to CO_2 is more important than for HCl groups, this indicating that the formation of carboxylic groups (both acid and anhydride, which decompose to CO_2 or $\text{CO}_2 + \text{CO}$, respectively [12]) predominates. On the contrary, when the concentration of DCI is high (for instance, see the change from carbon F-2.5 to F-10) the increase in the HCl peak is larger than for the CO_2 peak. The formation of acyl chloride groups C-COCl (decomposing at low temperature to CO and HCl) is now more favorable than the corresponding carboxylic C-COOH groups.

The amount of oxygen and chlorine surface groups decomposing at high temperature also increases with increasing concentration of DCI. As in the case of low temperature groups the formation of oxygen surface groups (in this case decomposing to CO) is favored at low concentrations of DCI, whereas the formation of C-Cl bonds is favored at high concentrations of DCI. On the other hand, the wide band (without defined peaks) observed at temperatures above 400°C indicates that the structures formed exhibit a wide range of thermal stability.

It is important to highlight the advantages of DCI in respect to NaClO for the oxidation of granular activated carbon. Carbon F was oxidized in previous tests with commercial bleach, as received and diluted to 10, 25 and 50v%. Although both chemicals, DCI and NaClO , permit the introduction of oxygen and chlorine surface groups, the main problem found with NaClO is the very limited reproducibility in the degree of oxidation (change in weight) of the sample. Additionally, the oxidation rate of bleach is low and a decrease in the pH of the solution produces a massive decomposition of ClO^- and the

subsequent change in concentration along the experiment. Oxidation rate with DCI (pH does not change with concentration), on the contrary, is approximately constant since it is controlled by the hydrolysis of N-Cl bonds in the molecule.

Figure 2 suggests that a heat treatment at 400°C would decompose selectively the low temperature groups evolving as CO₂ and HCl. However, their removal would leave behind reactive carbon atoms on the surface of the carbon, which would chemisorb oxygen when the carbon is in contact with air. This re-oxidation can be avoided if the treatment is carried out under a flow of propene. As shown in a previous work [8], the cracking of propene at 250-400°C produces radicals that would become bonded to the reactive carbon atoms of the surface, with the subsequent stabilization. In order to gradually eliminate the low temperature groups evolving as CO₂ and HCl and to prepare a carbon with groups evolving only high temperature, the carbon with the highest degree of oxidation, F-10, has been heat treated at 200, 250 and 300°C under a flow of propene.

Table 1 includes the data for the changes produced by the heat treatment on the porosity of the carbons. The first thing to note is that there is an increase in the volume of micropores (for instance, compare carbons F10 and F10-200) due to the thermal decomposition of functional groups, but there is a change in the tendency at 300°C for both V₀(CO₂) and V₀(N₂) because the amount of carbon deposited along the propene cracking is increasing and it produces a partial blocking of the porosity. This variation in the volume of micropores is in agreement with the mass of carbon; thus, if carbon F10 is taken as reference, this carbon loses 1 and 2wt% with the treatment at 200 and 250°C, respectively but it gains 1wt% at 300°C.

Figure 5 includes the TPD profiles for the carbons obtained after the treatment of carbon F10 under a flow of propene. The plots indicate that the oxygen functional groups of carbon F10 decomposing at a temperature lower than the one used in the treatment have been lost, the rest remaining unaltered. Only an additional decrease in groups evolving as CO is seen in carbon F10-300 because there was a carbon deposit partially covering the carbon surface. The more important and unexpected results were found for the HCl profiles: the low and high temperature chlorine functional groups decrease drastically when the carbon is heated under a flow of propene at a temperature as low as 200°C and the groups disappear at 250 and 300°C. The FTIR spectra corroborate this decrease since Figure 4 shows that the bands C-Cl at 1400 and 540 cm^{-1} disappears in the spectrum of carbon F10-250. The C-O band at 1700-1730 cm^{-1} is also lost, since there is loss of CO₂ groups. As it can be appreciated, the spectrum for carbon F10-250 is more similar to carbon F than to carbon F10.

The large decrease in the evolution of HCl for carbon F10-200 and the lack of groups evolving as HCl in the other carbons heat treated with propene (Figure 5c) cannot be due to the carbon deposit. As it was shown in [8] the cracking of propene on a carbon at 200°C was almost nil and, as shown in Figure 5b, there are no modifications in the high temperature CO profiles. It is rather probable that propene induces the rupture of C-Cl bonds because it facilitates the evolution of chlorine as HCl. This assumption is in agreement with previous works showing that the thermal stability of the C-Cl groups is a function of the amount of hydrogen of the carbon [4]. Since HCl molecules are evolving, the capture of H atoms is needed besides the rupture of the C-Cl bond and it is easier to get it from propene than from the solid carbon. It is important to note that the

carbon F was prepared at 850°C and, consequently, the hydrogen content is low, 0.6wt%.

3.2 Interaction of water with the carbon surface

Functional groups modify the hydrophilic character of the carbon. Figure 2 showed that the amount of surface oxygen and chlorine groups increase simultaneously with the concentration of DCI, this making difficult to separate the individual effect on the adsorption of water. However, some conclusions can be deduced when the data for the oxidized and propene treated carbons are compared.

Figure 6 includes the water adsorption isotherms for some selected carbons. The shape for the isotherm on carbon F is typical of activated carbons containing a low amount of surface groups and the evolution observed when oxidizing with DCI is similar to that found for other oxidizing agents such as nitric acid [15]: the increase in the degree of oxidation increases the amount of water adsorbed at low relative pressures (the carbon surface becomes more hydrophilic). The contrary occurs for the propane treatment. Thus, carbon F10-250 is less hydrophilic than carbon F10-200, which is similar to carbon F1. The proportion of groups evolving as CO₂ and HCl is almost nil in carbon F10-250 but there are more groups evolving to CO than in carbon F1. On the other hand, the number of groups leading to CO₂ in carbon F10-200 is similar to carbon F1, but the number of groups providing HCl is nil in the former and high in F1. It seems then that the groups evolving to CO₂ play a more important role in the hydrophilicity of the carbon than groups giving CO and HCl.

A more global view is possible when the number of the so-called primary centers of adsorption a_0 [16], obtained from the adsorption of water, is plotted versus the amount

of groups evolving to CO_2 , Figure 7. All carbons, both oxidized and heat treated under propene, fit a straight line going through the origin. Since the amount of groups leading to CO and HCl covers a wide range, the linear plot indicates that the groups decomposing to CO_2 (mainly carboxylic) interact more strongly with water molecules than the rest of the surface groups. The larger effect of groups evolving to CO_2 in respect to those decomposing to CO in the adsorption of water at low relative pressures was shown for other series of activated carbons [15]. The results presented here also show that the effect of C-Cl groups in the carbons is also small. Similar conclusions have been reached when activated carbons were treated with gaseous chlorine, since the adsorption isotherm for water on the chlorinated carbon is almost coincident with that for the treated with ethylene [17].

The interaction of water with the carbon surface has also been studied by immersion calorimetry. Table 1 collects the values of immersion enthalpy of the carbons in water, and it shows that it increases with oxidation and decreases with increasing temperature of propene treatment. This indicates the importance of specific interactions in addition to the non-specific ones in the values of ΔH_w . The best fit of ΔH_w with all parameters tested is the amount of CO_2 evolved upon decomposition of oxygen surface groups and Figure 8 shows the linear relationship. In this case the straight line cuts the ordinate in a value that could be considered as an estimate of the non specific interactions contribution to ΔH_w . Again, this plot indicates that the contribution of the groups decomposing to CO and HCl is very small. The lack of effect of chlorine groups was shown by MacDonald et al. [2,18] since the enthalpy of immersion of activated carbon in water was directly related to its content in oxygen and independent of chlorine treatment.

3.3 Interaction of ammonia with the carbon surface

The mechanism of adsorption of ammonia on an activated carbon is similar to that of other gases, micropore filling. However, in the application of this type of adsorbents in air purification the adsorption of ammonia occurs at room temperature and low concentration, this corresponding to the first stages of the adsorption process, before the actual filling of micropores takes place. For the adsorption to occur at an adequate proportion it needs the presence of functional groups in the adsorbent surface able to interact specifically with ammonia molecules. This work presents a study of the effect of oxygen and chlorine surface groups on: i) the adsorption isotherm of ammonia at low relative pressures and ii) the breakthrough curves using a flow of 1000 ppm of ammonia.

Figure 9 includes the adsorption isotherms of ammonia at 25°C for some selected carbons. The saturation pressure of ammonia at this temperature is 1002 kPa and only data up to a relative pressure $P/P_0 = 0.03$ have been registered. The isotherms show the important role of the surface chemistry of the carbon on the adsorption of ammonia at low relative pressures (for instance, $P/P_0 \sim 0.005$) since the amount adsorbed increases with oxidation although the volume of micropores decreases (see Table 1). The differences among the carbons become lower at higher relative pressures because the pore volume and the pore size distribution become more and more important.

Figure 10 includes the breakthrough curves for all activated carbons, and the low capacity of carbon F is to be noted. A small amount of ammonia is detected in the effluent as from the first moments of the experiment and the concentration increases fast after 2 min. Oxidation with DCI drastically increases the retention capacity of the

carbon and the treatment under a flow of propene reduces the breakthrough time of the column. The role of the surface functional groups in the removal of ammonia is clearly shown since the high surface area ($1370 \text{ m}^2/\text{g}$) and micropore volume ($0.53 \text{ cm}^3/\text{g}$) of carbon F do not contribute much to the removal of ammonia at the experimental conditions used (take into account that the breakthrough experiments were carried in the absence of humidity, required for the removal of ammonia to be more effective [19]). On the other hand, the increase in breakthrough time when comparing carbon F with carbons F1 or F2.5, is noteworthy, the increase being less important for carbon F10. Figure 2 indicated that the formation of C-Cl bonds was less important than the formation of oxygen groups for carbons F1 and F2.5, the contrary being the case for carbons F5 and F10. Consequently, the oxygen surface groups have a larger contribution to the removal of ammonia than the chlorine surface groups.

The breakthrough time for the heat-treated carbons decreases when the groups are partially removed. It seems that the groups evolving to CO_2 (mainly coming from carboxylic groups) are the more effective in the elimination of ammonia and that the influence of groups decomposing to CO and HCl is small. This idea is supported by: i) there is an important decrease in the breakthrough time between F10 and F10-250; the TPD profiles (Figure 5) show that whereas almost all groups evolving to CO_2 and HCl have been removed from F10 to F10-250, all groups decomposing at high temperature to CO are maintained, and; ii) the breakthrough times for F1 and F10-200 are similar; Figures 2 and 5 show that the amount of groups evolving to CO_2 are similar while there are clear differences in CO and HCl groups. The role of the surface acidity of the carbon (mainly provided by carboxylic groups) in the removal of basic species such as ammonia has been reported in previous works [1,20] and it has to be noted that a usual

way to study the surface acidity of silica and alumina-based catalysts is the TPD of ammonia [21].

Although the surface groups evolving as CO_2 are the more important in providing specific interactions with ammonia molecules, their role on the adsorption isotherms and breakthrough plots is not the same. The capacity for breakthrough of ammonia at 100 ppm has been calculated from the plots in Figure 10 and the resulting values have been plotted in Figure 11 as a function of the amount of ammonia adsorbed at $P/P_0 = 0.005$ (from the adsorption isotherms in Figure 9). The linear relationship indicates that the surface functional groups affect in the same way the ammonia uptake, although the amount adsorbed in the dynamic tests is lower. This shows that the non-specific interactions are governing the adsorption in the static process whereas the specific interactions are practically the only responsible for the increase in the breakthrough of carbon F when is oxidized with DCI.

4. Conclusions

The treatment of an activated carbon with an aqueous solution of DCI produces a simultaneous chemisorption of oxygen and chlorine, the formation of chlorine groups being more important when the concentration of DCI is high, the formation of oxygen groups predominating at low concentrations. Consequently, the use of an aqueous solution of DCI is to be preferred to a mixture of chlorine and oxygen in gas phase or to a solution of NaClO when there is a need for introducing both types of surface groups in an activated carbon. All chlorine functional groups have direct C-Cl bonds instead of C-O-Cl bonds.

The treatment with a flow of propene at 200-300°C in addition to decomposing the unstable oxygen surface groups at that temperature it removes all chlorinated groups, even those that are stable at temperatures as high as 900°C. It seems that propene provides the hydrogen required to produce HCl more easily than the fixed hydrogen of the carbon, thus promoting the cleavage of the C-Cl bonds. Consequently, it is not possible to obtain an activated carbon with only stable (high temperature) oxygen and chlorine groups by oxidation with DCI and subsequent heat treatment under propene.

Oxidation with aqueous DCI increases the hydrophilic character of the activated carbon, as deduced from the increase in the amount adsorbed of water at low relative pressures and from the immersion calorimetry data. In the same way, the retention capacity of ammonia increases with oxidation and the groups evolving as CO₂ are the more important in the specific interaction of the carbon surface with both water and ammonia, the interaction of the C-Cl groups not being significant. The effect of the surface functional groups in the breakthrough behavior of the oxidized carbons is very important since it may be up to twenty times higher than for the original carbon.

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References

- [1] T.J. Bandoz, C. Petit, J. Colloid Interface Sci. 338 (2009) 329-345.
- [2] J.A.F. MacDonald, M.J.B. Evans, S. Liang, S.E. Meech, P.R. Norman, L. Pears, Carbon 38 (2000) 1825-1830.
- [3] A.F. Perez-Cadenas, F.J. Maldonado-Hódar, C. Moreno-Castilla, Carbon 41 (2003) 473-478.

- [4] B.R. Puri, in: P.L. Walker (Ed.), *Chemistry and Physics of Carbon*, Marcel Dekker, Inc. New York, 1970, pp. 191- 282.
- [5] B. Cagnon, X. Py, A. Guillot, J.P. Joly, R. Berjoan, *Microporous and Mesoporous Materials* 80 (2005) 183-193.
- [6] M.L. Pinnsky, H.C. Hu, *Environmental Sci. Technol.* 15 (1981) 423-430.
- [7] C.M. Cepeda-Jimenez, M.M. Pastor-Blas, J.M. Martin-Martinez, P. Gottschalk, *J. Adhesion Sci. Technol.* 6 (2002) 257-283.
- [8] M. Goncalves, M. Molina-Sabio, F. Rodriguez-Reinoso, *J. Analytical and Applied Pyrolysis* 89 (2010) 17-21.
- [9] H. Marsh, F. Rodríguez-Reinoso, *Activated Carbon*, Elsevier, Amsterdam, 2006.
- [10] J. Silvestre-Albero, C.G. Salazar, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, *Colloids Surf. A Physicochem. Eng. Asp.* 187-188 (2001) 151-165.
- [11] E. Papier, R. Lacroix, J.B. Donnet, G. Nansé, P. Fioux, *Carbon* 33 (1995) 63-72.
- [12] P. Burg, D. Cagniant, in: L.R. Radovic (Ed.), *Chemistry and Physics of Carbon*, CRC Press Boca Raton, 2008, pp. 129- 176.
- [13] J.L. Figueiredo, M.F.R. Pereira, *Catal.Today* 150 (2010) 2-7.
- [14] H. Hu, B. Zhao, M.A. Hamon, K. Kamaras, M.E. Itkis, R.C. Haddon, *J. Am. Chem. Soc.* 125 (2003) 14893-14900.
- [15] F. Rodríguez-Reinoso, M. Molina-Sabio, M.A. Muñecas, *J. Phys. Chem.* 96 (1992) 2707–2713.
- [16] F. Rouquerol, J. Rouquerol, K. Sing, *Adsorption by Powders & Porous Solids: Principles Methodology and Application*, Academic Press, London, 1999.
- [17] J.A.F. MacDonald, M.J.B. Evans, *Carbon* 40 (2002) 703-707.
- [18] M.J.B. Evans, E. Halliop, S. Liang, J.A.F. MacDonald, *Carbon* 11 (1998) 1677-1682.
- [19] L.M. Le Leuch, T.J. Bandosz, *Carbon* 45 (2007) 568-578
- [20] C.C. Huang, H.S. Li, C.H. Chen, *J. Hazardous Materials* 159 (2008) 523-527.
- [21] C.M. Hidalgo, H. Itoh, T. Hattori, M. Niwa, Y. Murakami, *J. Catal.* 85 (1984) 362-369.

Table 1. Some characteristics of activated carbons

Carbon	Δm (%)	$V_0(N_2)$ (cm ³ g ⁻¹)	$V_0(CO_2)$ (cm ³ g ⁻¹)	ΔH_w (J/g)
F	0	0.53	0.42	41
F1	7	0.50	0.40	52
F2.5	12	0.42	0.37	57
F5	16	0.41	0.35	60
F10	20	0.39	0.34	67
F10-200	-	0.49	0.37	52
F10-250	-	0.48	0.40	46
F10-300	-	0.46	0.38	43

Figure captions

Figure 1. Molecular structures of sodium dichloroisocyanurate along with the parent compound isocyanuric acid.

Figure 2. TPD profiles of carbons oxidized with DCI corresponding to desorption of (a) CO₂, (b) CO and (c) HCl.

Figure 3. Curve-fitted Cl_{2p} of XPS spectra for carbon F10.

Figure 4. FTIR spectra of some carbons.

Figure 5. TPD profiles of carbons heat-treated in propene corresponding to desorption of (a) CO₂, (b) CO and (c) HCl.

Figure 6. Water adsorption isotherms at 25°C for some (a) oxidized and (b) propene heat-treated activated carbons.

Figure 7. Relationship between the primary active adsorption centers and oxygen groups evolving as CO₂.

Figure 8. Relationship between the water immersion enthalpy and oxygen groups evolving as CO₂.

Figure 9. Ammonia adsorption isotherms at 25°C for some activated carbons.

Figure 10. Ammonia breakthrough curves for oxidized and propene heat-treated activated carbons.

Figure 11. Amount of ammonia adsorbed at P/P₀= 0.005 vs ammonia breakthrough capacity of activated carbons.

Figure captions

Figure 1. Molecular structures of sodium dichloroisocyanurate along with the parent compound isocyanuric acid.

Figure 2. TPD profiles of carbons oxidized with DCI corresponding to desorption of (a) CO₂, (b) CO and c) HCl.

Figure 3. Curve-fitted Cl_{2p} of XPS spectra for carbon F10.

Figure 4. FTIR spectra of some carbons.

Figure 5. TPD profiles of carbons heat-treated in propene corresponding to desorption of (a) CO₂, (b) CO and c) HCl.

Figure 6. Water adsorption isotherms at 25°C for some activated carbons.

Figure 7. Relationship between the primary active adsorption centers and oxygen groups decomposed as CO₂.

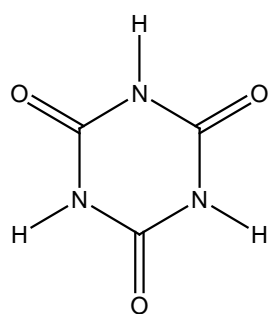
Figure 8. Relationship between the water immersion enthalpy and oxygen groups decomposed as CO₂.

Figure 9. Ammonia adsorption isotherms at 22°C for some activated carbons.

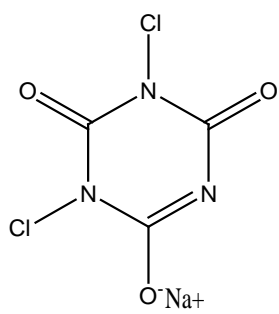
Figure 10. Ammonia breakthrough curves for oxidized and propene heat-treated activated carbons.

Figure 11. Amount of ammonia adsorbed at P/P₀= 0.005 vs ammonia breakthrough capacity of activated carbons.

Figure 1

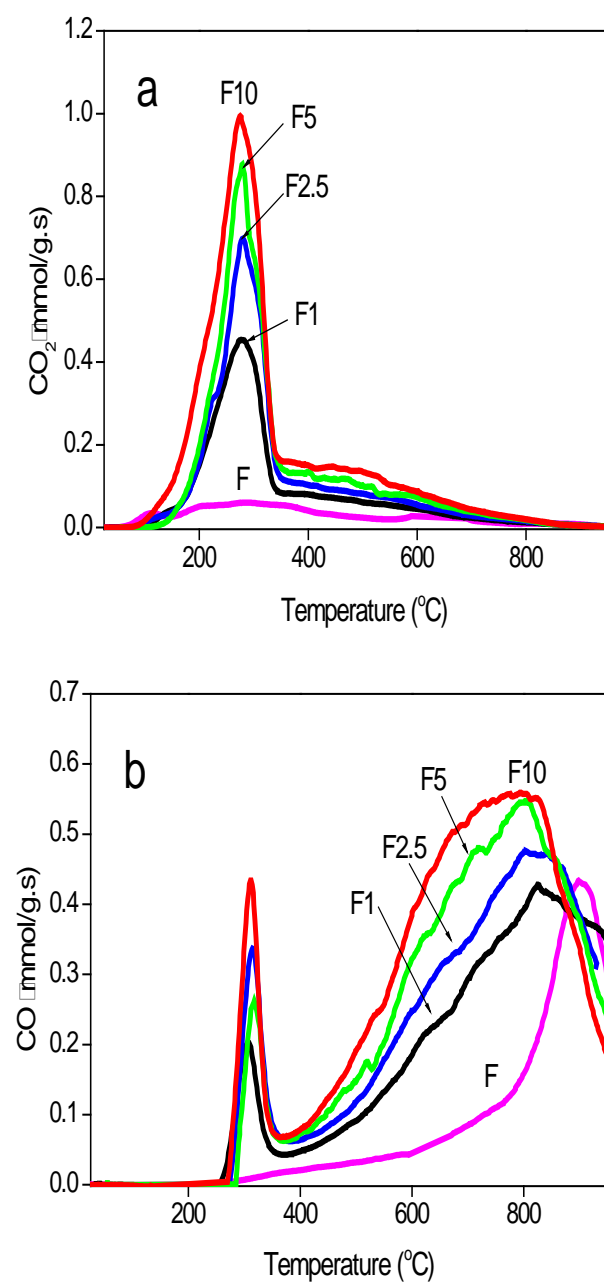


Isocyanuric acid



Sodium dichloroisocyanurate

Figure 2



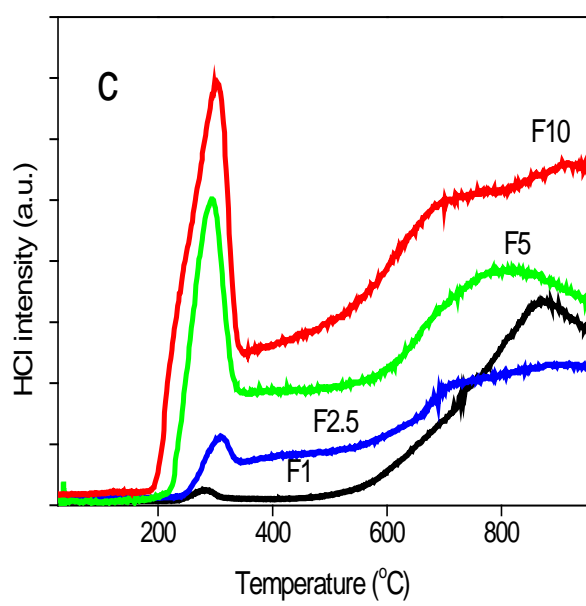


Figure 3

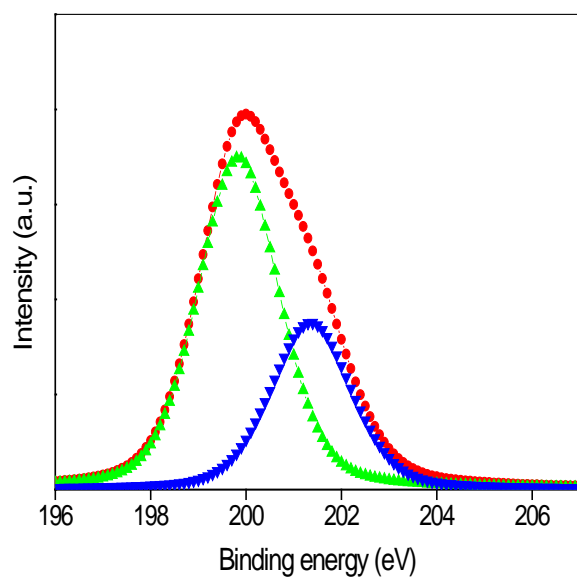


Figure 4

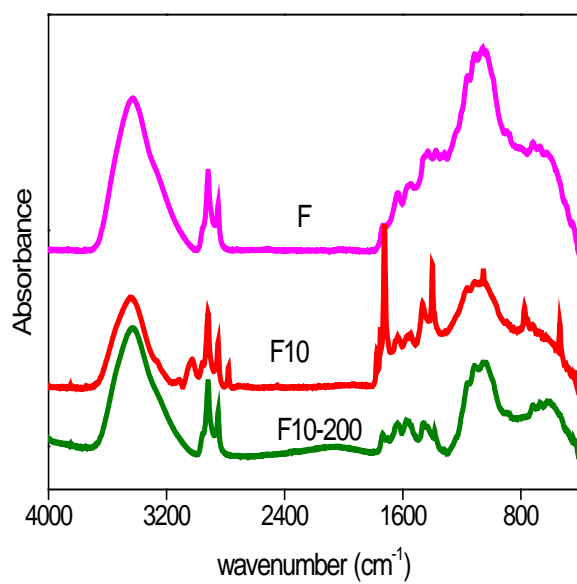
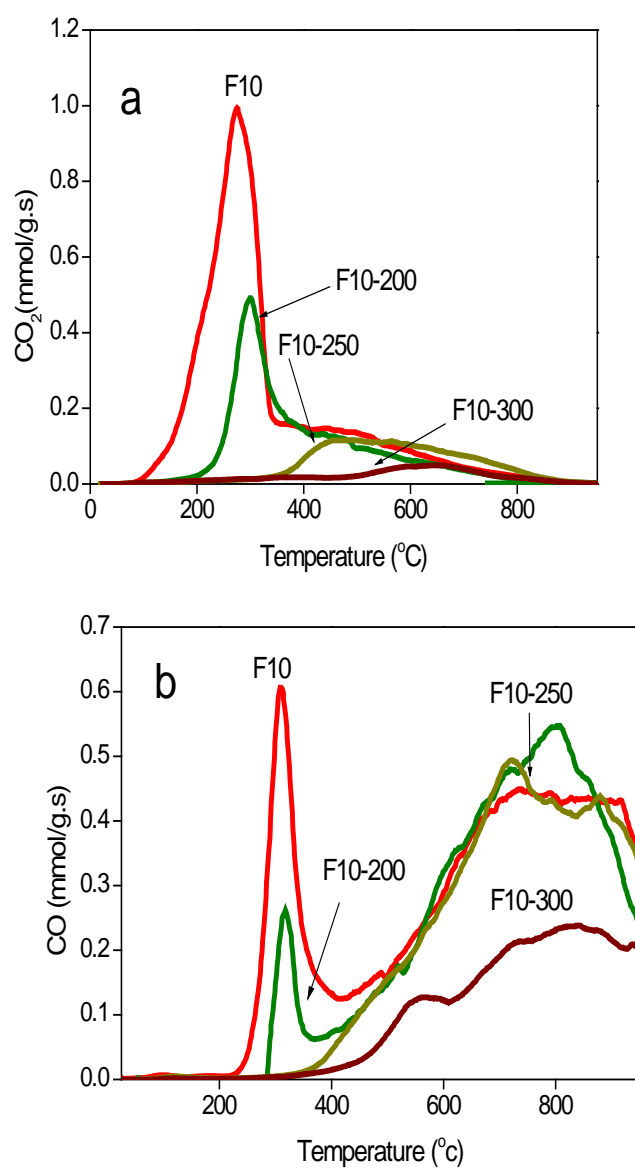


Figure 5



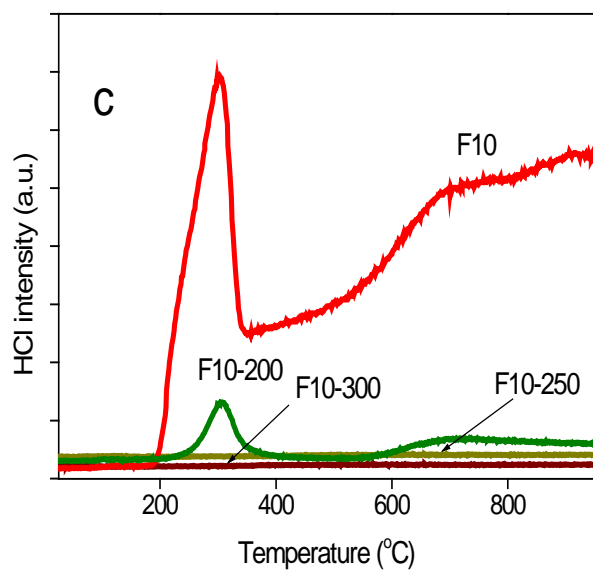


Figure 6

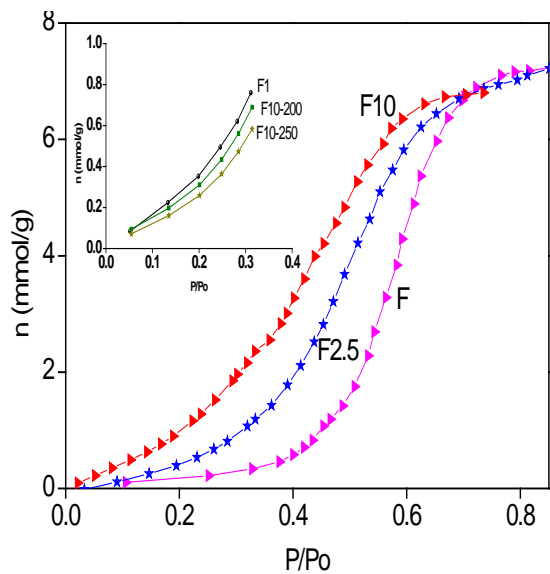


Figure 7

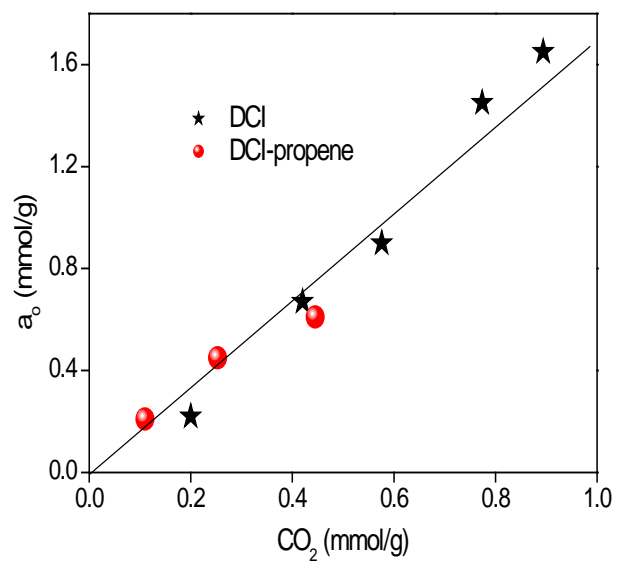


Figure 8

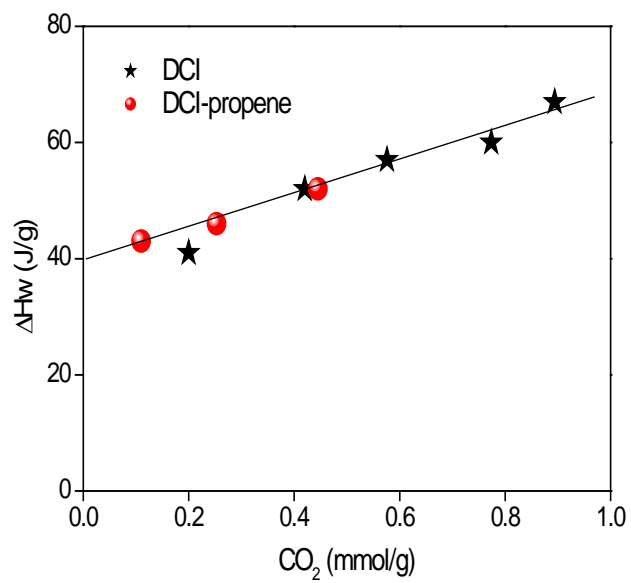


Figure 9

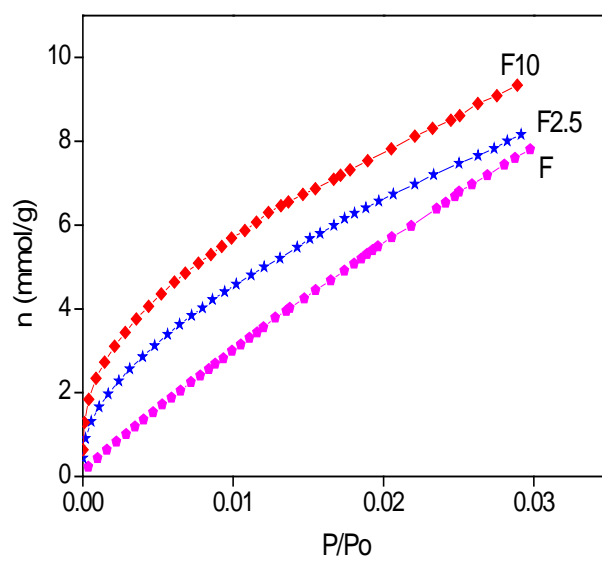


Figure 10

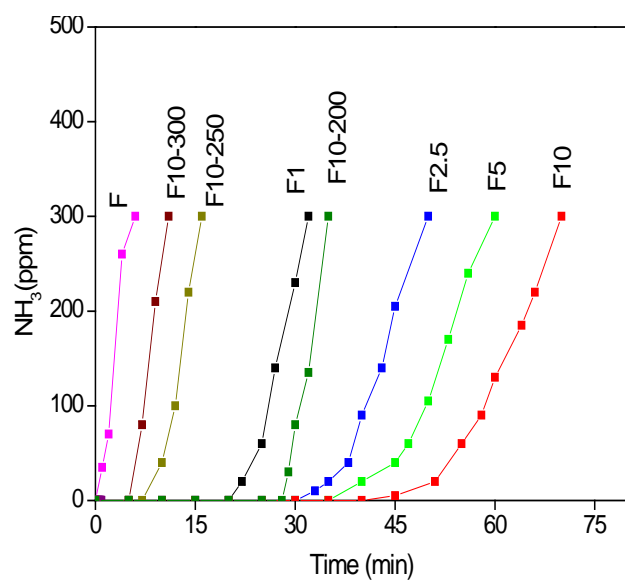


Figure 11

